Anodic Film Growth on Tungsten Studied with EQCM and EIS

M.-G. Vergé, C.-O. A. Olsson, and D. Landolt

Laboratoire de Métallurgie Chimique, Département des Matériaux, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne EPFL, Switzerland

Introduction

Anodic oxide films have been subjected to extensive work but their growth mechanism is still not completely understood. Several different growth mechanisms have been suggested. Essentially, film growth can be limited either in the film itself through high field ion migration (HFM) or by a reaction at one of the film interfaces (IFM). These models were recently discussed in detail by Olsson et al. [1] who measured film thickness changes on PVD-deposited Cr using the electrochemical quartz crystal microbalance (EQCM), which provides a time-resolved *in situ* estimate of mass changes. By comparing experimental data to theoretical simulations, these authors found the IFM to be more successful in predicting film growth for different initial passive film thicknesses, in a range from 0.5 to 3 nm on Cr. The thickness of passive films on Cr is limited by the onset of transpassive dissolution. To study the effect of initial film thickness on the growth behavior as a criterion for distinguishing IFM and HFM, metals such as Ta, Ti or W are more suitable. The aim of the present study is to investigate the film growth kinetics of anodic films on W using the EQCM and to compare experimental results with the prediction of IFM and HFM.

Experimental

EQCM experiments were performed with sputter deposited films of W on AT-cut quartz crystal using a deaerated 0.1M H_2SO_4 + 0.4M Na_2SO_4 electrolyte. Samples were initially polarized to $2V_{SHE}$ to form a stable passive film. This was followed by a rapid increase to $5V_{SHE}$, a potential that was maintained for 60 min. Finally, the potential was stepped to $8V_{SHE}$ and kept for 60 min. The net sample current and mass change was measured using the EQCM. The thickness change of the film was calculated from

$$\Delta d = \frac{1}{\rho} \left(\frac{qM_w}{nF} + \Delta m_{EQCM} \right) \qquad (1)$$

where Δm_{EQCM} is the measured mass change, n is the valency. q is the charge (C/cm^2), M_w is the tungsten molar mass, F is the faraday's constant, and the density, ρ (WO_3) is 716 $ng/nm\,cm^2$. Impedance spectroscopy analyses were also performed to estimate thickness of the oxide film as a function of time for 2 and $5V_{SHE}$.

Results

The mass change and current density measured during a potential step from 2 to $5V_{SHE}$ are shown in Fig. 1. From the EQCM data, it is seen that practically all current measured during the potential step serves for film growth. In the long-term limit, the current stabilizes at a steady state value while the mass decreases linearly with time. From the mass and current, it is possible to calculate a thickness change from eq. 1. The film thickness was also estimated from high frequency capacity (C) determined by electrochemical impedance spectrometry (EIS). Results obtained from the following expression $C = \varepsilon_r \varepsilon_0 A / d$ where A is surface area, ε_r=35 [2] is the dielectric constant, and ε_0 is the permittivity of free space,

are shown in Fig. 2. Changing the potential from 2 to $5V_{SHE}$ leads to a steep increase in film thickness after which it stays constant. The same results were found by Macdonald et al [2]. The data of Fig.1 show that under these conditions the mass of the electrode decreases, indicating that anodic dissolution takes place. A more quantitative comparison shows that anodic dissolution can not account for all of the charge passed and therefore an additional anodic reaction must take place, such as decomposition of water. Additional experiments will be conducted to quantify the contributions of the different anodic reactions as a function of applied potential and to get a better understanding of anodic film properties on tungsten.

Conclusion

The present data show that anodic film growth on W resulting from a potential change can be monitored *in situ* with the EQCM. A comparison of the growth curves at different initial film thickness with theoretical simulations based on the IFM and HFM suggests that the latter describes better film growth kinetics on W contrarily to the behavior observed for the much thinner films on Cr. At a constant potential of $5V_{SHE}$ metal dissolution, at constant film thickness, was observed jointly with a second anodic reaction involving oxidation of the solvent.

References

1. C.-O. A. Olsson, D. Hamm, D. Landolt, J. Electrochem. Soc. **147**, 2563 (2000)
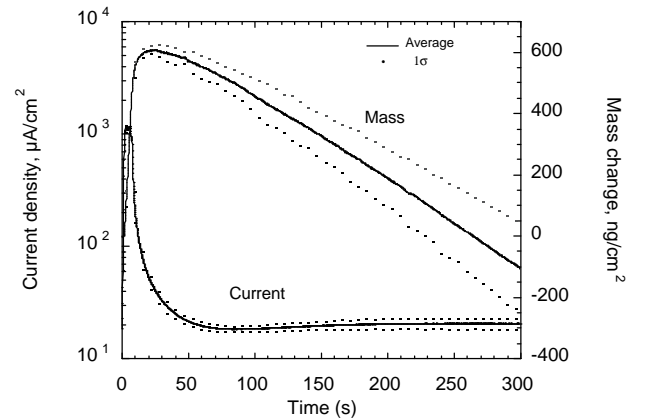2. D. D. Macdonald, E. Sikora, J. Sikora, Electrochim. Acta, **43**, 2851 (1998)

Fig. 1. Average and standard deviation based on three experiments for current and mass responses recorded at 400mV/s from 2 to 5 V_{SHE}.
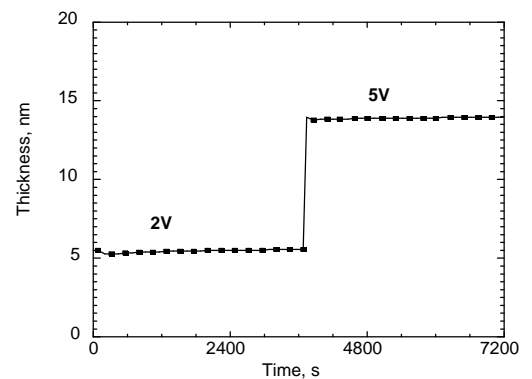

Fig. 2. Thickness estimated by EIS for 2 and $5V_{SHE}$.